$$\text{IV} + \text{F}^- \overset{K}{\rightleftharpoons} \text{V or Va} \xrightarrow{k} \text{products}$$

$$\frac{1}{k_F} = \frac{1}{k} + \frac{1}{k}K[\text{F}^-] \quad (1)$$

added fluoride ion) to the fluoride-catalyzed reaction (*cf.* ref 42).

A plot of $1/k_F$ against $1/[F^-]$ is linear (Figure 5), except towards the intercept where the negative salt effect of sodium fluoride may be important. From the value at the intercept we calculate $10^2k = 4.5$ sec^{-1} for breakdown of the intermediate to products, and from it and the slope we calculate an equilibrium constant $K = 30$ l. $mole^{-1}$.

Fluoride ion also catalyzes the hydrolysis in aqueous dioxane; comparison with Tillett's results for hydrolysis in dioxane–water (60:40 v/v) at 0°, where $10^4k_\psi = 0.36$ sec^{-1}, shows that 0.005 *M* potassium fluoride increases the rate 70-fold.[5] This reaction was not studied in detail in aqueous dioxane, but fluoride ion is a much more effective catalyst in these solvents than in water, presumably because it is less solvated than in water.[18]

Because of solubility problems, the fluoride ion catalyzed hydrolysis of diphenyl sulfite was not studied in detail, but spectrophotometric measurements suggest that fluoride ion catalyzes the spontaneous hydrolysis. However, the hydrolysis of diethyl sulfite is not catalyzed by fluoride ion, and potassium hydrogen fluoride is a relatively ineffective catalyst, and hydrogen fluoride is less effective than the strong mineral acids (Table IV and ref 4). Therefore, it seems that ethoxy is not a good enough leaving group to be displaced by fluoride ion, just as neither it, nor aryloxy, are displaced by chloride ion from sulfur. Wiberg has made the generalization that, for substitutions at a carbonyl carbon atom, one base will not displace appreciably stronger bases,[43] and this generalization apparently applies also to sulfite hydrolysis.

The high nucleophilicity of fluoride ion towards *o*-phenylene sulfite and the relatively high stability of the intermediate (V or Va) are not unexpected, because sulfur–fluorine bonds are strong; *e.g.*, sulfonyl fluorides are much less reactive than the chlorides towards water.[44]

Despite the unreactivity of fluoride ion toward diethyl sulfite, hydrogen fluoride is a much more effective catalyst than would be expected if it acted solely as a proton donor, because it is only slightly dissociated,[45] and its protonating power, as measured by Hammett's acidity function, is considerably less than that of a strong acid; *e.g.*, for 1 *M* acids perchloric acid protonates a nitroamine approximately 30 times more strongly than does hydrofluoric acid.[46]

The catalyzed reaction presumably involves attack of the hydrogen bifluoride ion upon the conjugate acid of the ester.

Acknowledgments.—We thank Mr. A. J. Bond for preliminary experiments on diphenyl sulfite, and Miss Julia M. Bunton for technical assistance.

(42) F. R. Duke, *J. Am. Chem. Soc.*, **69**, 3054 (1947).

(43) K. B. Wiberg, *ibid.*, **77**, 2519 (1955).
(44) C. G. Swain and C. B. Scott, *ibid.*, **75**, 246 (1953).
(45) H. H. Broene and T. de Vries, *ibid.*, **69**, 1644 (1947).
(46) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

The Mechanism of the Alkyl Sulfide–Sulfinic Acid Reaction. The Direction of Cleavage of Unsymmetrical Sulfides[1a]

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In the recently discovered reaction of alkyl sulfides with *p*-toluenesulfinic acid the alkyl sulfide is cleaved and one of its alkyl groups is oxidized (eq 1). Previous studies have suggested that the rate-determining step of this reaction is an elimination (eq 2) which is formally similar to the key step in the pyrolysis of either sulfoxides or amine oxides. We have now determined the preferred direction of cleavage, and, therefore, of elimination, for a series of unsymmetrical sulfides by measurement of the relative amounts of the two possible alkyl thiolsulfonates formed as products in the different cases. The results are compared with those of Cope, *et al.*, for the pyrolytic elimination of a series of unsymmetrical amine oxides and are found to be surprisingly similar. The significance of this finding for the mechanism of the rate-determining step of the sulfide–sulfinic acid reaction is discussed, and it is concluded that eq 7 is probably a more accurate representation of that step than is eq 2.

A new reaction between alkyl sulfides and *p*-toluenesulfinic acid has recently been described.[2] In this reaction the sulfide is cleaved and one of its alkyl groups is oxidized, the over-all course of the reaction being as shown in eq 1. Previous study[2b] of the mechanism of the reaction has suggested that the rate-determining step is the unimolecular elimination shown in eq 2. The formal relationship of reaction 2 to such other eliminations as the pyrolyses of amine oxides[3,4] (eq 3) and sulfoxides[5,6] (eq 4) is readily apparent.

$$5\text{ArSO}_2\text{H} + (\text{RCH}_2)_2\text{S} \longrightarrow 2\,\text{ArS(O)–SAr} + \text{ArS(O)–SCH}_2\text{R} + \text{RCHO} + 3\text{H}_2\text{O} \quad (1)$$

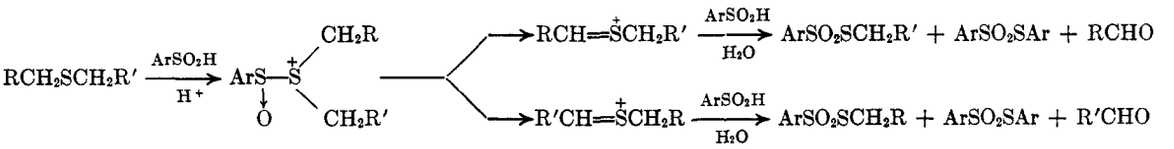
Ar = *p*-$CH_3C_6H_4$

(1) (a) This research supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AFOSR-106-65. (b) Research participant in National Science Foundation Research Participation for College Teachers Program, Oregon State University, 1964.

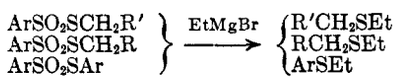
(2) (a) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 2390 (1962); (b) J. L. Kice and E. H. Morkved, *ibid.*, **85**, 3472 (1963); (c) J. L. Kice and E. H. Morkved, *J. Org. Chem.*, **29**, 1942 (1964).
(3) D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **76**, 5740 (1954).
(4) (a) A. C. Cope, T. T. Foster, and P. H. Towle, *ibid.*, **71**, 3929 (1949); (b) A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *ibid.*, **79**, 4729 (1957); (c) A. C. Cope, N. A. LeBel, H. H. Lee, and W. R. Moore, *ibid.*, **79**, 4720 (1957).
(5) D. J. Cram and C. A. Kingsbury, *ibid.*, **82**, 1810 (1960).
(6) C. Walling and L. Bollyky, *J. Org. Chem.*, **29**, 2699 (1964).

CHART I

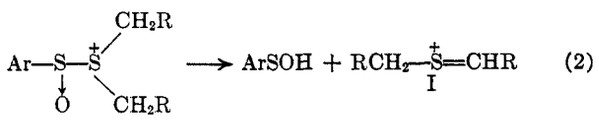
SCHEMATIC OUTLINE OF THE REACTION OF AN UNSYMMETRICAL SULFIDE IN THE SULFIDE–SULFINIC ACID REACTION AND THE ANALYSIS OF THE THIOLSULFONATE FRACTION

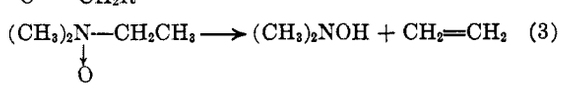


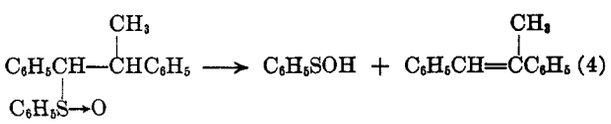
Analysis



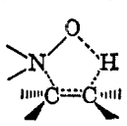
sulfide mixture analyzed by glpc



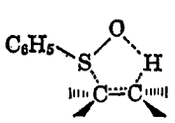




The amine oxide and sulfoxide pyrolyses are known to be quite stereospecific *cis* eliminations,[4,5] the geometry of the transition state being best described as an essentially planar quasi-five-membered ring (II). Cope,



IIa



IIb

et al.,[4c] have determined the preferred direction of elimination for the pyrolyses of a series of open-chain unsymmetrical amine oxides of the type $R_1R_2CH_3$-N→O. Except when one of the alkyl groups has a β-aryl substituent, there is little preference for elimination in a particular direction, and the two possible olefins are formed in a ratio approximately equal to the ratio of available β-hydrogens in the two alkyl groups. When a β-aryl substituent is present, there is a marked preference for elimination to occur in that direction to give the conjugated olefin.

Although the suggested rate-determining step of the sulfide–sulfinic acid reaction (eq 2) is formally similar to the amine oxide and sulfoxide pyrolyses, the substitution at the α-position of a positively charged trivalent sulfur for a neutral tetrahedral carbon could conceivably result in significant differences in the preferred direction of elimination in unsymmetrical sulfides. A determination of the nature of such differences and the magnitude thereof should assist one in drawing a more precise picture of the rate-determining transition state of the sulfide–sulfinic acid reaction than has been possible before and should thereby permit a more detailed description of its mechanism.

The present paper reports the results of a study of this type. In it the preferred direction of elimination for a series of unsymmetrical sulfides has been determined and the results are compared with those of Cope, *et al.*,[4c] for the pyrolysis of amine oxides. The implications for the mechanism of the sulfide–sulfinic acid are then discussed.

Results

Under the reaction conditions used for the sulfide–sulfinic acid reaction ion I, once formed, undergoes immediate hydrolysis (eq 5).[2b] The mercaptan liber-

ated in the hydrolysis then reacts very rapidly with sulfinic acid, with the stoichiometry shown in eq 6.[2b]

Accordingly, the preferred direction of elimination for an unsymmetrical sulfide RCH_2SCH_2R' may, in principle, be determined either from the relative amounts of the two aldehydes, RCHO and R'CHO, produced or from the relative amounts of the two alkyl thiolsulfonates, $ArSO_2SCH_2R'$ and $ArSO_2SCH_2R$. Because most aldehydes undergo extensive condensation under the strongly acidic conditions used for the sulfide–sulfinic acid reaction, while the various alkyl thiolsulfonates are not noticeably altered by the same reaction conditions, estimation of the preferred direction of elimination by measurement of the mole ratio of alkyl thiolsulfonates was the method chosen.

p-Toluenesulfinic acid was the arylsulfinic acid used in all of the present studies. After reaction of the sulfinic acid with the unsymmetrical sulfide, the thiolsulfonate fraction, consisting of *p*-tolyl *p*-toluenethiolsulfonate ($ArSO_2SAr$) and the two alkyl *p*-toluenethiolsulfonates, was separated from the other products by chromatography. The relative amounts of the two alkyl *p*-toluenethiolsulfonates in this fraction were then determined by one of two methods, depending on the unsymmetrical sulfide involved.

The principal method used involved the treatment of the crude thiolsulfonate fraction with an excess of ethyl magnesium bromide. As outlined in Chart I, this cleaves the various thiolsulfonates and converts their thioalkyl groups to the corresponding alkyl ethyl sulfides.[7] The relative amounts of these were then determined by vapor phase chromatography. Trial experiments with known mixtures of the various alkyl thiolsulfonates showed that the cleavage with the Grignard reagent gave in each case mole ratios of alkyl ethyl sulfides which agreed closely with those expected from the initial ratios of thiolsulfonates taken. The procedure thus does not lead to selective cleavage of one thioalkyl group in preference to the other.

(7) H. Gilman, L. E. Smith, and H. H. Parker, *J. Am. Chem. Soc.*, **47**, 851 (1925).

TABLE I

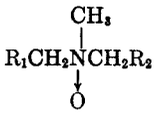
DIRECTION OF ELIMINATION IN SULFIDE–SULFINIC ACID REACTIONS OF UNSYMMETRICAL SULFIDES[a]

Sulfide (R_1SR_2)		$\frac{[ArSO_2SR_1]}{[ArSO_2SR_2]}$	Loss of H from R_1/loss of H from R_2	
R_1	R_2		Obsd	Statistical[b]
CH_3CH_2	$(CH_3)_2CH$	1.1	0.90	2.0
CH_3CH_2	$CH_3CH_2CH_2CH_2$	1.5	0.66	1.0
CH_3CH_2	$(CH_3)_2CHCH_2$	1.5	0.66	1.0
$CH_3CH_2CH_2CH_2$	CH_3	0.84	1.2	0.67
CH_3CH_2	$C_6H_5CH_2$	19	0.053	1.0
CH_3CH_2	p-$ClC_6H_4CH_2$	16	0.063	1.0
CH_3CH_2	p-$O_2NC_6H_4CH_2$	9.4	0.11	1.0

[a] All runs are at 70° in acetic acid–0.56 M water–0.6 M sulfuric acid as solvent. [b] Based solely on the number of available α-hydrogens

TABLE II

DIRECTION OF ELIMINATION IN THE PYROLYSIS OF AMINE OXIDES[a]



R_1	R_2	Composition of olefin mixture (%)	Loss of H from R_1/loss of H from R_2	
			Obsd	Statistical[b]
CH_3CH_2	$(CH_3)_2CH$	Propylene (59) Isobutylene (41)	1.4	2.0
CH_3CH_2	$CH_3CH_2CH_2$	Propylene (43) 1-Butene (57)	0.75	1.0
CH_3CH_2	$(CH_3)_2CHCH_2$	Propylene (44.1) 3-Methyl-1-butene (55.9)	0.79	1.0
CH_3CH_2	CH_3	Propylene (37.5) Ethylene (62.5)	0.60	0.67
CH_3	$C_6H_5CH_2$	Ethylene (1.3)	0.015	1.5

[a] Data from ref 4c. [b] Based solely on the number of available α-hydrogens in R_1 and R_2.

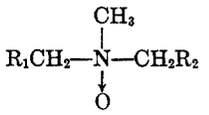
In the case of benzyl ethyl sulfide and also of two *para*-substituted benzyl ethyl sulfides, the relative amounts of ethyl and benzyl *p*-toluenethiolsulfonates could be determined without resorting to cleavage of the thiolsulfonate fraction. This was done by comparing the integrated intensity of the nmr singlet for the CH_2S group of the benzyl ester with that of the quartet for the CH_2S group of the ethyl ester.

The results for the sulfide–sulfinic acid reactions of the various unsymmetrical alkyl sulfides studied are shown in Table I.

Discussion

From Table I we see that, for all cases except the three alkyl benzyl sulfides, the elimination ratio is not greatly different from that expected on a purely statistical basis from the relative numbers of hydrogens on the two carbons adjacent to the sulfide sulfur. On the other hand, in the three benzylic sulfides there is a marked preference for elimination in the direction of the aryl group, loss of a benzylic hydrogen being favored by a factor of 10 to 20. That such a preference would exist had already been suggested by earlier kinetic studies on the relative reactivity of various sulfides.[2b] These showed that, while the rates of reaction of a considerable number of sulfides $(RCH_2)_2S$ with *p*-toluenesulfinic acid could be correlated with σ^* for R, the reactivity of benzyl sulfide (R = C_6H_5) was substantially greater than expected from the σ^* value for phenyl. The present results thus provide satisfying corroboration of our earlier deductions[2b] from purely kinetic data.

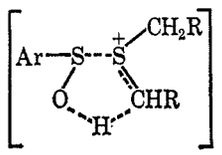
As noted above, Cope, *et al.*,[4c] have determined the preferred direction of elimination for the pyrolysis of a series of open-chain unsymmetrical amine oxides of the type



That portion of their results particularly pertinent to the present study is shown in Table II. Comparison of the data in Tables I and II shows that the two reactions display only relatively small differences in behavior. Thus, in the ethyl–benzyl system the amine oxide exhibits about a fourfold greater preference for loss of a benzyl proton than does the sulfide–sulfinic reaction. In the ethyl–isopropyl and ethyl (or *n*-butyl)–methyl systems elimination in the direction of the more highly alkylated α-carbon competes somewhat more effectively in the sulfide–sulfinic acid reaction than it does in the amine oxide pyrolysis. However, in either system the difference in elimination ratio between the two reactions is at most a factor of 2.

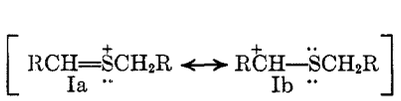
Previous kinetic studies of the sulfide–sulfinic acid reaction[2a] have established that the rate-determining transition state is formed, with elimination of a molecule of water, from a proton and a molecule each of sulfinic acid and sulfide. Rate measurements[2b] on benzyl-α-d_2 sulfide have shown that the reaction is subject to a large kinetic isotope effect (k_H/k_D = 5.2). This large an isotope effect clearly demonstrates that an α-C–H bond in the sulfide is broken in the rate-determining step. These facts, together with the

fairly sizeable negative value of ρ^* for the reaction (-1.85) obtained from a plot of rates for $(RCH_2)_2S$ *vs.* σ^* for R, have previously[2b] seemed best accommodated by a mechanism having eq 2 as its rate-determining step. Implicit in this suggestion of eq 2 as the rate-determining step was the idea that scission of the S–S bond in $ArS(O)\overset{+}{S}(CH_2R)_2$ was synchronous with scission of the α-C–H bond, the transition state for reaction 2 being pictured as III. In III the fragment



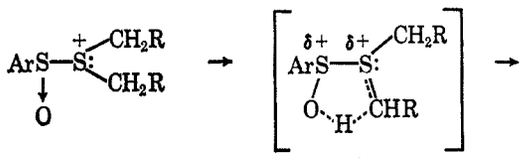
III

derived from the sulfide should have a fairly close structural kinship to the ion $RCH{=}\overset{+}{S}CH_2R$ (I) shown as one of the products of eq 2. There also seems good reason to believe that resonance form Ib makes a significant contribution to the structure of I.[8] Accordingly, the



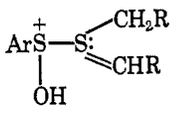
energy of the sulfide-derived moiety in III, and of III itself, should be significantly dependent on the ability of the group R to assist in stabilizing an adjacent carbonium ion. In a comparison of elimination ratios for amine oxide pyrolysis and the sulfide–sulfinic acid reaction for such systems as ethyl–isopropyl or *n*-butyl–methyl, one would therefore expect the sulfide–sulfinic acid reaction to show a considerably greater tendency for elimination to occur in the direction of the more highly alkylated α-carbon. However, as Tables I and II indicate, any effect of this type is at best a most modest one. Moreover, similar considerations would also predict that in the ethyl–benzyl system the sulfide–sulfinic acid reaction should show a much greater preference than the amine oxide pyrolysis for elimination of the benzylic proton. This is contrary to what is observed. In our opinion the results in Tables I and II therefore seem to indicate that III, with its exactly synchronous breaking of the S–S and C–H bonds, is not the proper representation for the transition state of the sulfide–sulfinic acid reaction.

In considering suitable alternatives to III it is important to remember that, while the large kinetic isotope effect requires an α-C–H bond be broken in the rate-determining step, it does not require that the sulfur–sulfur bond in $ArS(O)\overset{+}{S}(CH_2R)_2$ necessarily be broken in the same step. Thus eq 7, involving scission of the C–H bond without scission of the S–S bond is a perfectly acceptable alternative to eq 2 for the rate-determining step. (An intermediate, VI,



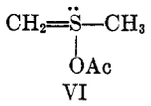
transition state

V



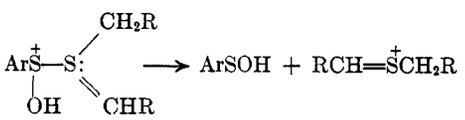
IV

related to IV, and involving a similar valence shell expansion of sulfur, has been implicated by Oae and co-workers in the Pumerer reaction.[10]) All that is



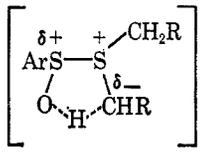
VI

then required is that IV, once formed, rapidly yield I by dissociation. That such a reaction (eq 8) would



occur very readily is perfectly plausible. The structure (V) postulated as the transition state for eq 7 seems much more compatible than III with the observed similarity of the elimination ratios in Tables I and II, while at the same time being consistent with the previously reported[2b] kinetic isotope effect and ρ^* value.

Finally, we might note that the results with the two *para*-substituted benzyl sulfides in Table I appear to rule out any ylid-like alternatives to V, such as VII. Were the transition state to have structure VII,



VII

p-nitrobenzyl ethyl sulfide would show a greater preference for elimination of a benzylic proton than does benzyl ethyl sulfide. In actual fact, the reverse is true, loss of a benzyl proton being twice as strongly preferred for benzyl ethyl sulfide. This demonstrates that there is no increase in the electron density on the α-carbon on going from the sulfide to the transition state.

Experimental Section

Preparation and Purification of Materials.—*p*-Toluenesulfinic acid was prepared and purified according to previously published procedures.[11] The acetic acid used as solvent for the sulfide–sulfinic acid reactions was also purified by the procedure outlined earlier.[11]

Sulfides.—The following sulfides were purchased from commercial sources and were purified by careful fractional distillation:

(8) In the hydrolysis of a series of acetals, $RCH(OEt)_2$, the rate-determining transition state is considered to have considerable oxocarbonium character. Kreevoy and Taft[9] found a large dependence of hydrolysis rate on the ability of R to help stabilize a positive charge on the carbon adjacent to oxygen, showing that in the oxygen counterpart of I a structure analogous to Ib is an important contributor.

(9) M. M. Kreevoy and R. W. Taft, *J. Am. Chem. Soc.*, **77**, 5590 (1955).

(10) S. Oae, T. Kitao, S. Kawamura, and Y. Kitaoka, *Tetrahedron*, **19**, 817 (1963).

(11) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

ethyl sulfide, bp 92°; ethyl isopropyl sulfide, bp 106–107°; and *n*-butyl methyl sulfide, bp 123°. *n*-Butyl ethyl sulfide, bp 144–145° (lit.[12] bp 144–145°), and isobutyl ethyl sulfide, bp 134° (lit.[13] bp 134–135°), were both synthesized, following standard procedures, from ethyl iodide and the appropriate mercaptan. Ethyl methyl sulfide, bp 65–66° (lit.[14] bp 66.6°), and ethyl *p*-nitrobenzyl sulfide,[15] mp 20–21°, were prepared by reaction of sodium ethanethiolate with methyl iodide and *p*-nitrobenzyl bromide, respectively. The crude ethyl *p*-nitrobenzyl sulfide was purified by an initial distillation followed by chromatography on alumina. The sulfide was eluted with hexane–benzene mixtures and, after removal of the elution solvents by distillation, it could be induced to crystallize by cooling it in the icebox. Benzyl ethyl sulfide,[16] bp 35–36° (0.15 mm), and *p*-tolyl ethyl sulfide,[16] bp 100–102° (11–12 mm), were prepared from the appropriate thiols and ethyl bromide.

p-Chlorobenzyl Ethyl Sulfide.—To 0.20 mole each of potassium hydroxide and *p*-chlorobenzyl mercaptan dissolved in ethanol was slowly added an ethanol solution containing 0.22 mole of ethyl bromide. After the addition was complete, the reaction mixture was refluxed for 9 hr. At the end of this time the reaction mixture was filtered to remove potassium bromide. The ethanol was removed from the filtrate by distillation and the residue was taken up in ether. The ether solution was washed once with aqueous sodium hydroxide, then several times with water, and dried over magnesium sulfate, and the ether was evaporated. The residue was distilled under reduced pressure: bp 129–131° (10 mm); yield, 15.5 g (42%).

Anal. Calcd for $C_9H_{11}ClS$: C, 57.89; H, 5.94. Found: C, 57.90; H, 5.61.

Thiolsulfonates.—Samples of certain of the thiolsulfonates formed as products of sulfide–sulfinic acid reactions were required for trial cleavage experiments with ethyl magnesium bromide. *p*-Tolyl,[11] *n*-butyl,[2b] and isopropyl[17] *p*-toluenethiolsulfonates were already available. **Ethyl *p*-toluenethiolsulfonate** was synthesized in 89% yield by the same procedure[2b] used for the *n*-butyl ester. When pure it melted at 30–31°.

Anal. Calcd for $C_9H_{12}O_2S_2$: C, 49.95; H, 5.59. Found: C, 50.12; H, 5.63.

Isobutyl *p*-toluenethiolsulfonate was prepared by the route used for the isopropyl ester.[17] A similar purification procedure was also employed.

Anal. Calcd for $C_{11}H_{16}O_2S_2$: C, 54.09; H, 6.60. Found: C, 54.4; H, 6.33.

Procedure for Alkyl Sulfide–*p*-Toluenesulfinic Acid Reactions.—A solution of *p*-toluenesulfinic acid (0.05–0.10 *M*) and the alkyl sulfide (0.1–0.2 *M*) in acetic acid–0.56 *M* water–0.6 *M* sulfuric acid was made up and deaerated at room temperature. The reaction was carried out by heating the deaerated solution to 70°. Suitable reaction times for each case were determined by rough preliminary kinetic studies on the various alkyl sulfide–*p*-toluenesulfinic acid reactions.

After the reaction was complete, the thiolsulfonate fraction was separated from the other products and excess unchanged sulfide by the procedures previously outlined.[2b,c] In the case of ethyl *p*-nitrobenzyl sulfide, rechromatography of a portion of the thiolsulfonate-containing fractions was necessary in order to remove some of the *p*-nitrobenzaldehyde also formed in the reaction.

Analysis of Thiolsulfonate Fraction. Nmr Method.—In the case of ethyl benzyl, ethyl *p*-chlorobenzyl, and ethyl *p*-nitrobenzyl sulfides the relative amounts of ethyl and benzyl *p*-toluenethiolsulfonates in the thiolsulfonate fraction could be determined by examining the nmr spectrum of a solution of the entire thiolsulfonate fraction and comparing the integrated intensity of the nmr singlet for the CH_2S group of the benzyl ester with that of the quartet for the CH_2S group of the ethyl ester. The CH_2 quartet of the ethyl ester is centered at τ 7.08. The methylene group resonances of the three benzyl esters are found at: benzyl, τ 5.84; *p*-chlorobenzyl, τ 5.84; and *p*-nitrobenzyl, τ 5.76.

Grignard Cleavage Method.—The thiolsulfonate fraction was dissolved in a small amount of ether, and the resulting solution was added slowly with efficient stirring to an ether solution containing a twofold molar excess of ethyl magnesium bromide. After the addition was complete, the reaction mixture was stirred for a short period of time at room temperature and was then heated for several hours. It was subsequently hydrolyzed with dilute sulfuric acid. The ether layer was separated, and the aqueous layer was extracted with several small portions of ether. The combined ether solutions were washed with aqueous sodium bicarbonate, then with water, and were finally dried over anhydrous sodium sulfate.

Depending on the amount of thiolsulfonate used and the volume of the final ether solution, the dried ether solution was either used directly for the gas chromatographic studies or was further concentrated by removal of a portion of the ether *via* careful fractional distillation. The relative amounts of the two ethyl alkyl sulfides resulting from cleavage of the alkyl *p*-toluenethiolsulfonates were then estimated by comparison of their relative glpc peak areas with those for known mixtures of the same ethyl alkyl sulfides in ether. The glpc work was done using a Perkin-Elmer Model 154 vapor refractometer equipped with a 6-ft Type-A column. Different column temperatures were used for different pairs of ethyl alkyl sulfides, but all were in the range 110–130°.

In each system a trial cleavage experiment was carried out using a known mixture of the appropriate pair of alkyl thiolsulfonates. Its purpose was to ensure that there was no preferential cleavage of one alkyl thiolsulfonate over the other and that the mole ratio of the two alkyl ethyl sulfides, as determined by glpc analysis, was equivalent to the mole ratio of the two alkyl *p*-toluenethiolsulfonates in the original sample. In several of these experiments *p*-tolyl *p*-toluenethiolsulfonate was included in the thiolsulfonate mixture taken for cleavage in order that the trial mixture would correspond exactly to that resulting from a sulfide–sulfinic acid reaction. The results of the various trial cleavages were as follows: $ArSO_2SEt$:$ArSO_2SBu$-*n*, 1.17:1.00 (Et_2S:EtSBu-*n* found, 1.21:1.00); $ArSO_2SEt$:$ArSO_2SCHMe_2$, 1.19:1.00 (Et_2S:$EtSCHMe_2$ found, 1.37:1.00); $ArSO_2SMe$:$ArSO_2SBu$-*n*, 1.32:1.00 (EtSMe:EtSBu-*n* found, 1.19:1.00); and $ArSO_2SEt$:$ArSO_2SCH_2CHMe_2$, 0.99:1.00 (Et_2S:$EtSCH_2CHMe_2$ found, 1.06:1.00). The mole ratio of sulfides found differs, even in the worst case, by only 12% from that expected from the mole ratio of thiolsulfonates taken. Clearly, there is no problem with selective cleavage. However, in treating the data obtained for cleavages of the thiolsulfonate fractions from the sulfide–sulfinic acid reactions these small differences were considered real, and appropriate small correction factors were used in calculating the mole ratio of alkyl thiolsulfonates from the glpc data on the sulfides.

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